

Speciation and Mobility of Zn and Cu in a truck farming soil contaminated by sewage irrigation

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Context

Phytoremediation is a rapidly growing bio-technology to remediate soils, sediments and solid wastes contaminated by heavy metals. The general objective of this program is to contribute to improve existing techniques and foster the development of spin-off technologies based on the knowledge and human-controlled modification of the molecular form of metals.

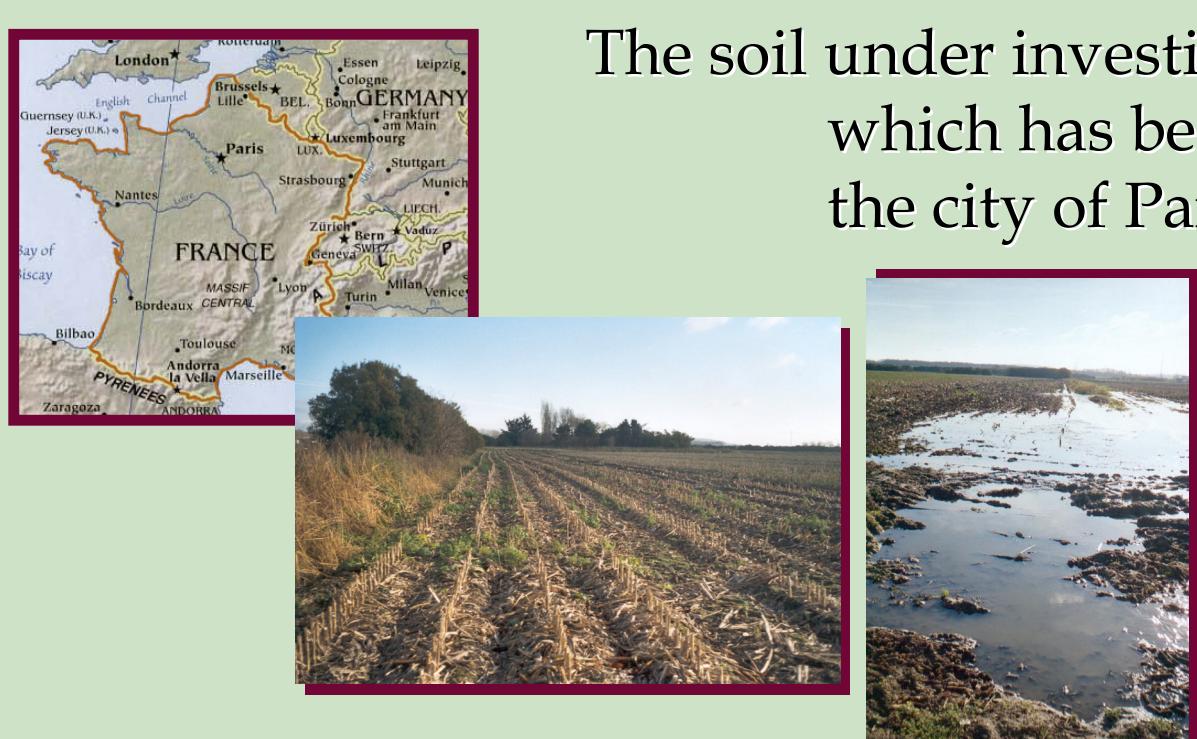


Phytoremediation pilot study

In the present study, the mobility and speciation of Zn and Cu in a contaminated soil is being studied before (risk assessment), during, and after phytoremediation (quality assessment).

The samples

The soil under investigation was collected at Pierrelaye, a large truck farming area, which has been irrigated for more than a century with sewage water from the city of Paris.



Soil characteristics

Bulk	Zn mg/kg	Cu mg/kg	Pb mg/kg	Fe mg/kg	P mg/kg	Ca mg/kg	K mg/kg	Al mg/kg	Si mg/kg
	1103	290	535	14269	2531	24228	4555	13019	185581

pH (in H₂O) 6.5

Mineralogy

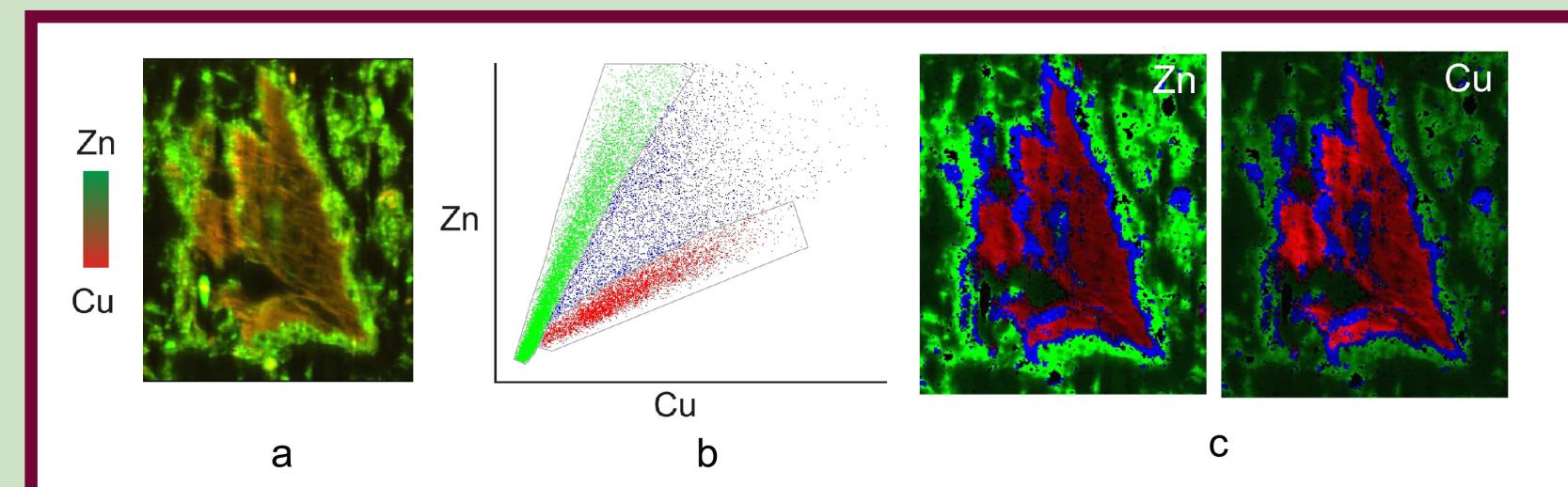
Elemental distribution (%)

Size fraction	wt. %	Quartz, Calcite, Albite, Microcline, Kaolinite, Muscovite
Sand	69%	17 18 15 25 20 23 34 27 79
Silt	23%	41 47 43 39 41 55 49 44 18
Clay	8%	42 35 42 36 39 22 17 29 3

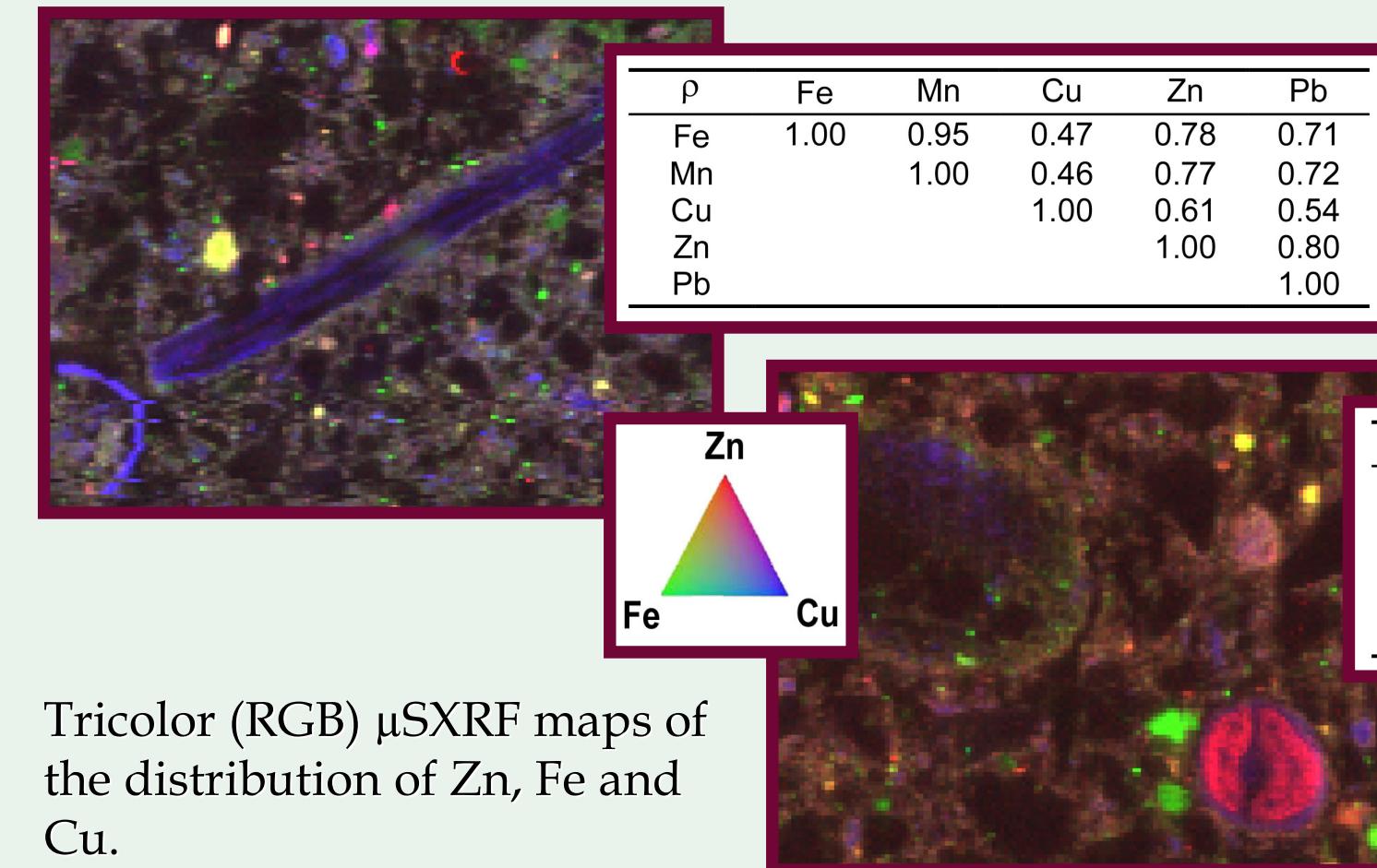
The soil was prepared for speciation studies as pressed pellets from the soil powder, and as micro-polished 30 µm-thick sections.

Distribution of Metals by µSXRF

Population-segmentation method to isolate metal species.
(a) Bicolour map of Zn (green) and Cu (red). (b) Zn vs. Cu scatterplot. (c) Greyscale maps for Zn and Cu coloured according to membership in the populations defined as in part b.



The large reddish (Cu-rich) area in the centre (a) was identified by light microscopy as organic matter with a reticular structure. There are two distinct populations (b) with roughly constant Zn/Cu ratio in each population. There are three regions (c), within the organic area, outside the organic area, and a border region. The brightness of each pixel is related to the Zn or Cu concentration. Both metals are present in all regions, but probably in different forms.



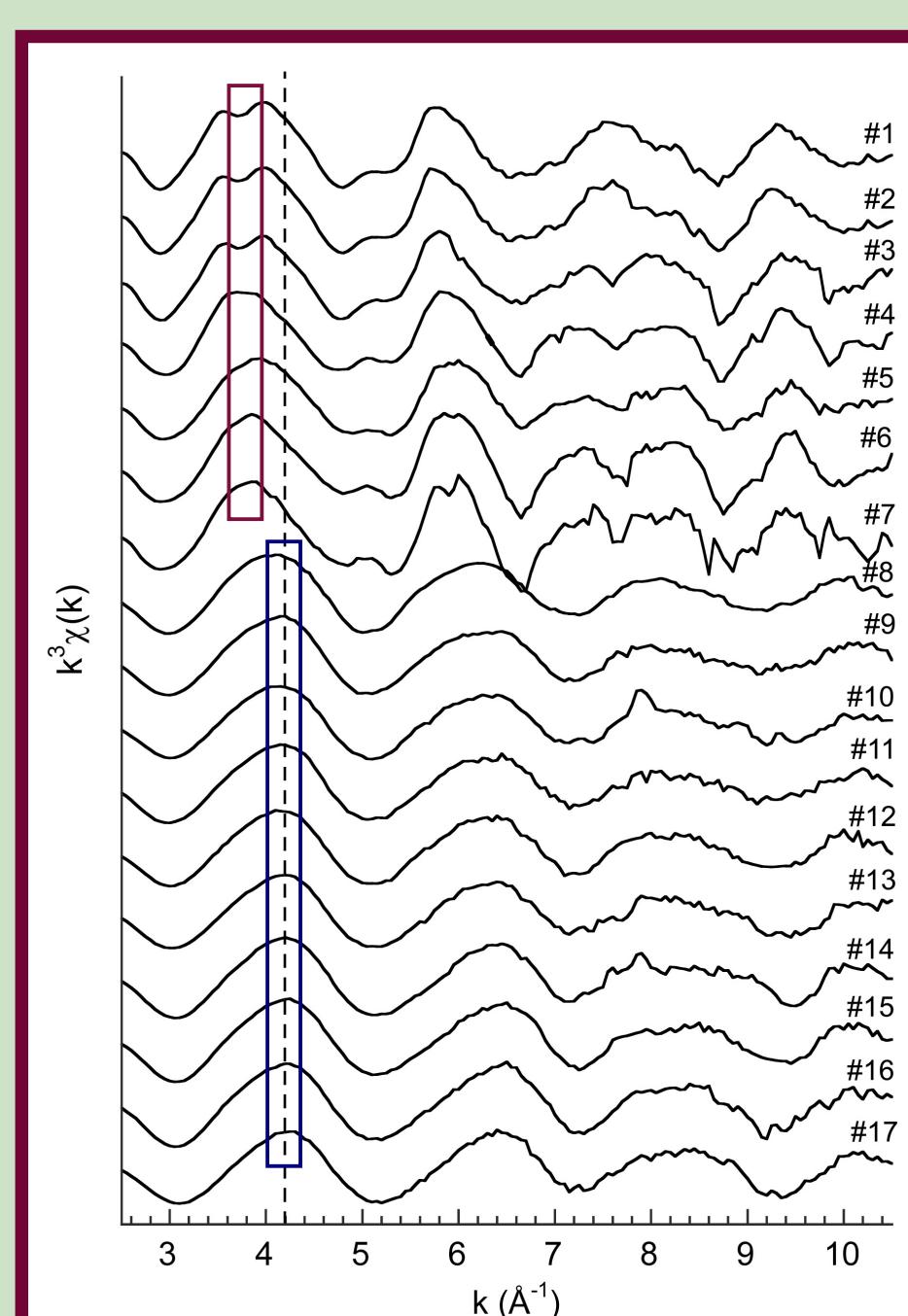
Zn is highly correlated with Fe suggesting an association with Fe oxides. In contrast, Cu is never highly correlated with Fe. The spatial distribution of Cu corresponds preferentially with the distribution of organic debris.

Elements are unevenly distributed and present in various forms.

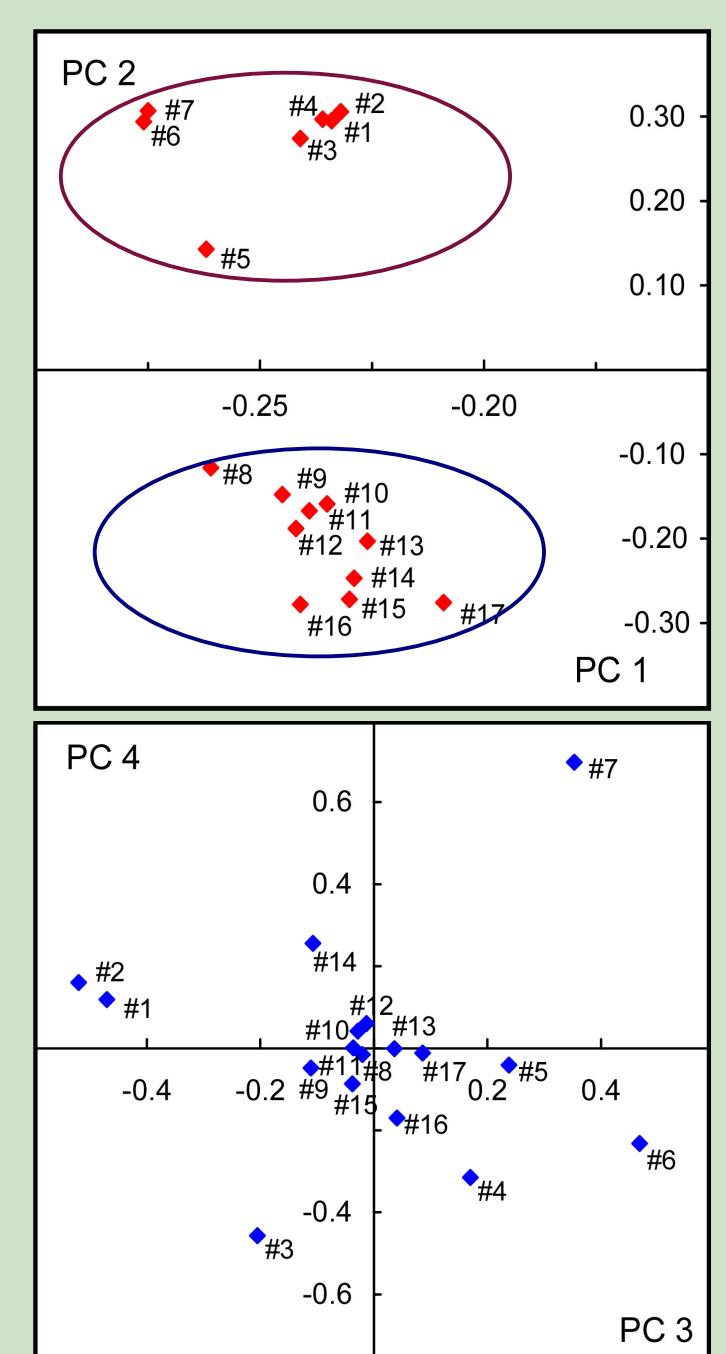
Number, Nature and Proportion of Zn Species at the micrometer scale by µEXAFS

Number by PCA analysis

Four principal components are sufficient to describe the set of 17 µEXAFS spectra, therefore four Zn species are predominantly present.



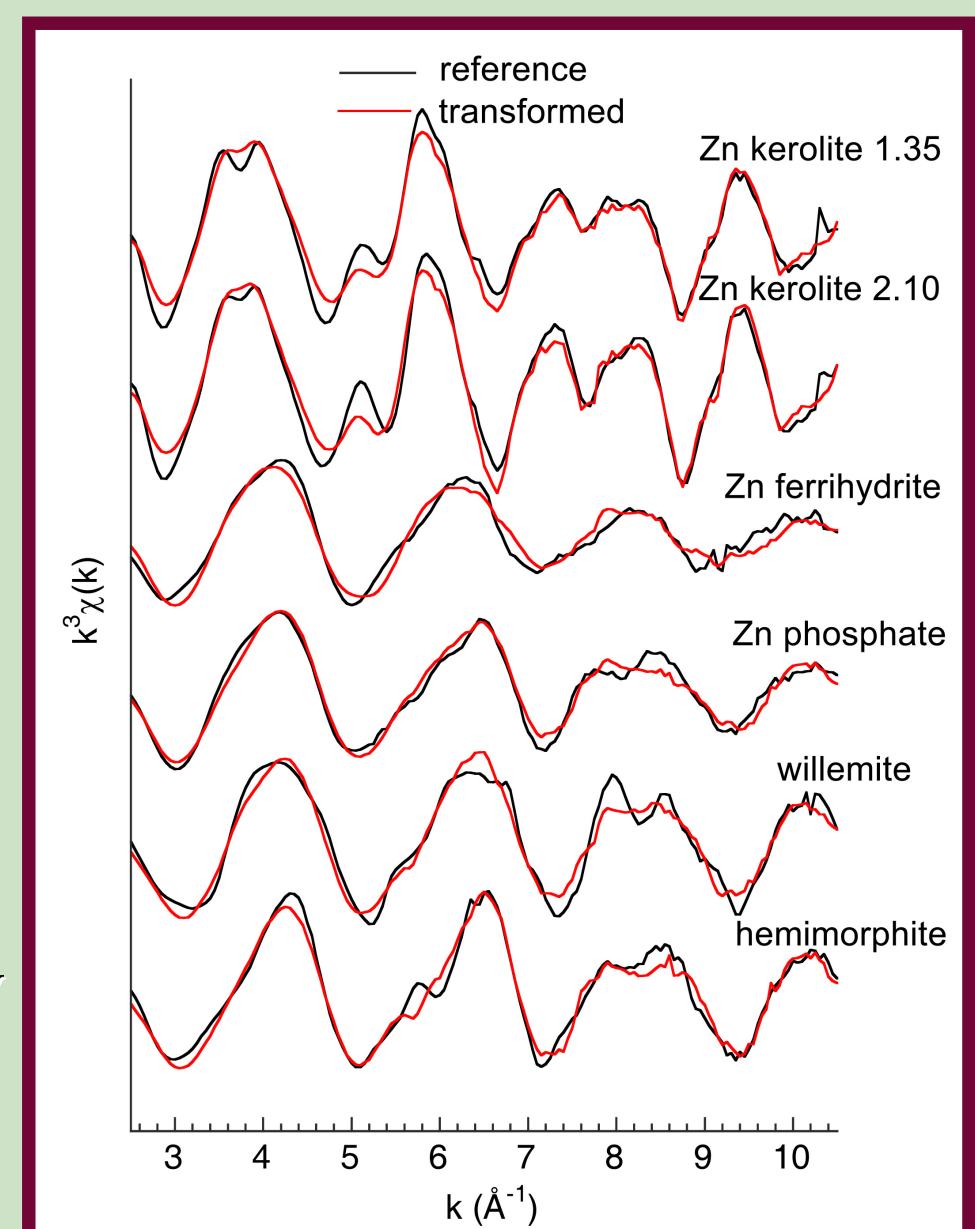
Zn K-edge µEXAFS spectra collected in different ROIs of the soil matrix.



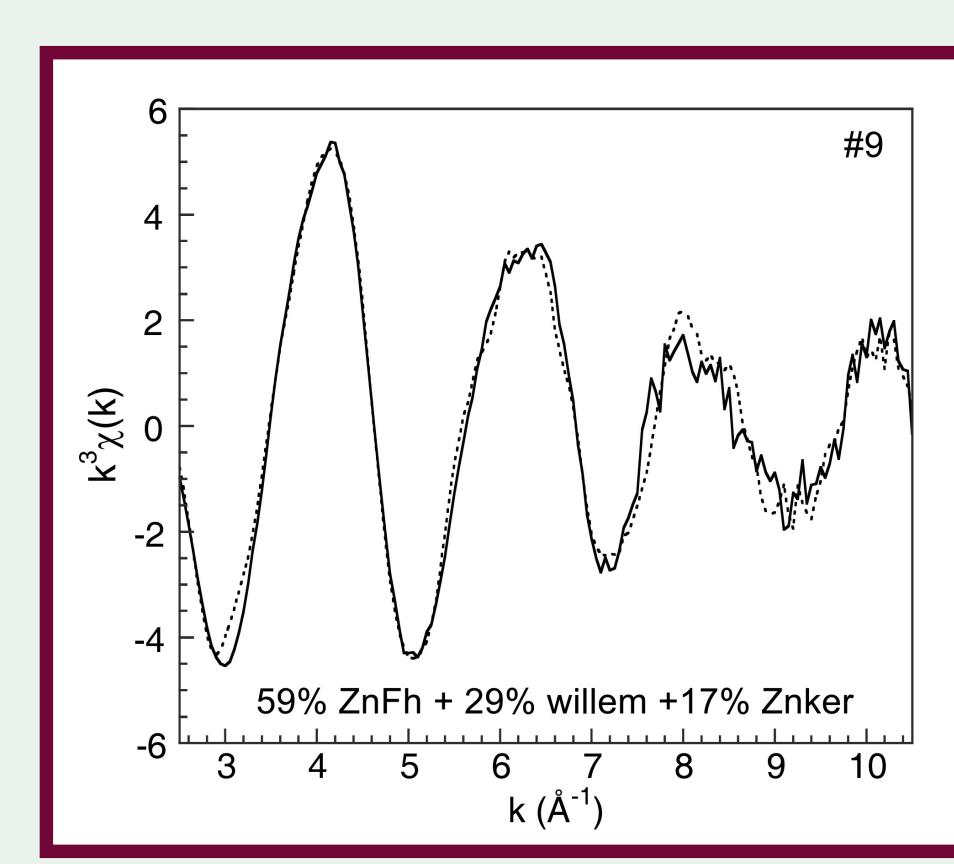
PC 1 vs. PC 2 and PC 3 vs. PC 4 plots of the amounts of PCs in µEXAFS spectra.

Nature by Target transformation

The visual examination of the EXAFS oscillations clearly shows two populations. Quantitative spectral analysis revealed that Zn is octahedrally coordinated in one population and tetrahedrally coordinated in the other.

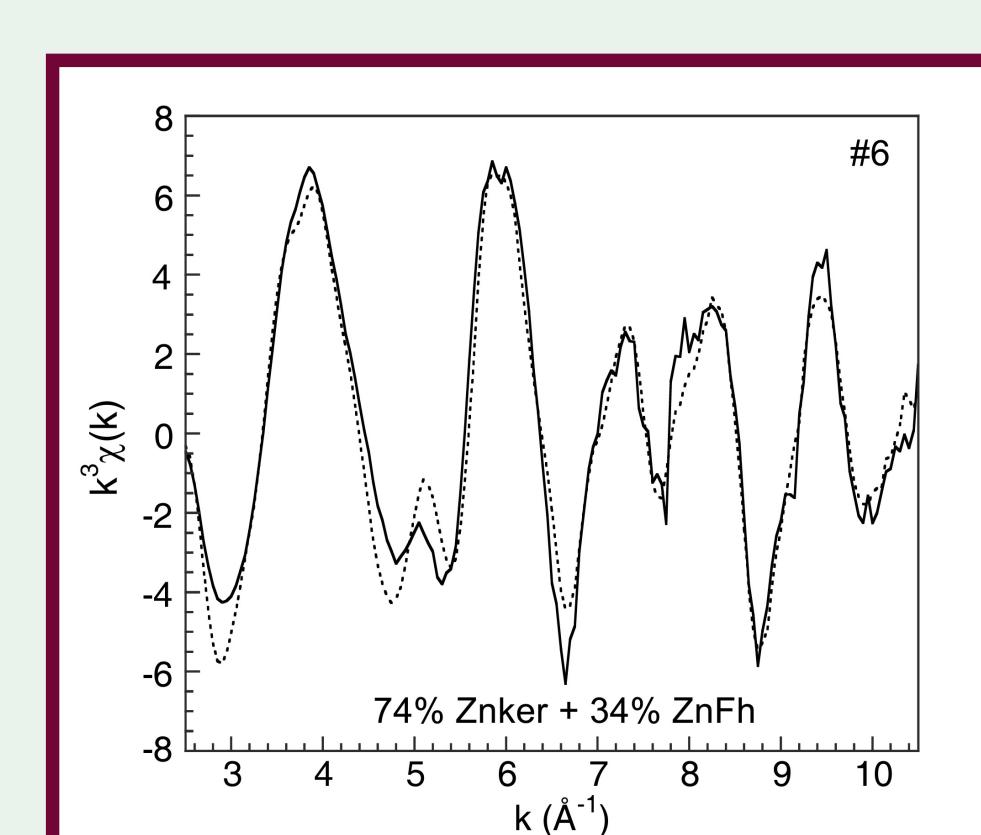


Target transformation using four PCs.



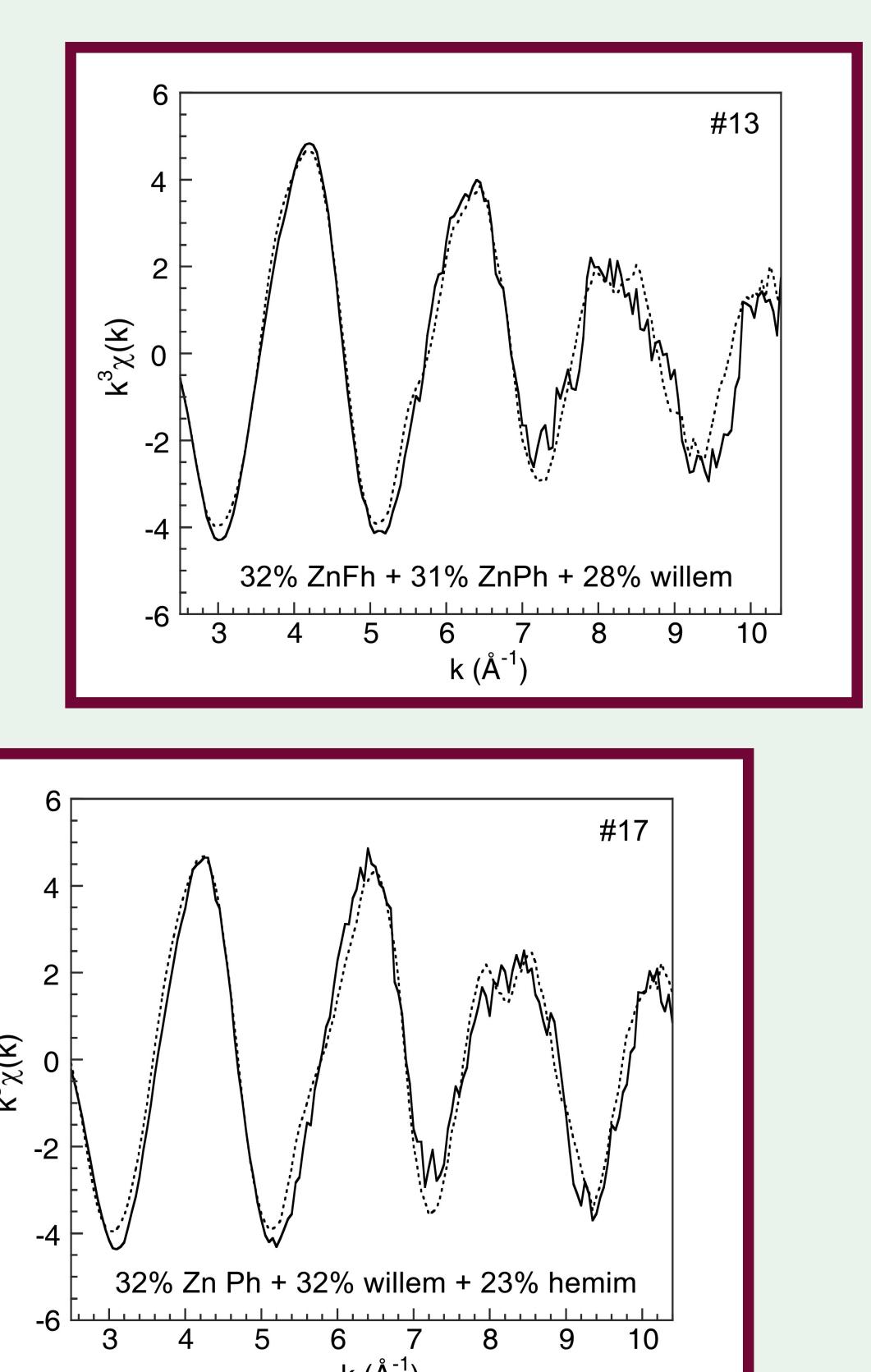
Linear combination fitting of several µEXAFS spectra.

Proportion by LCFitting



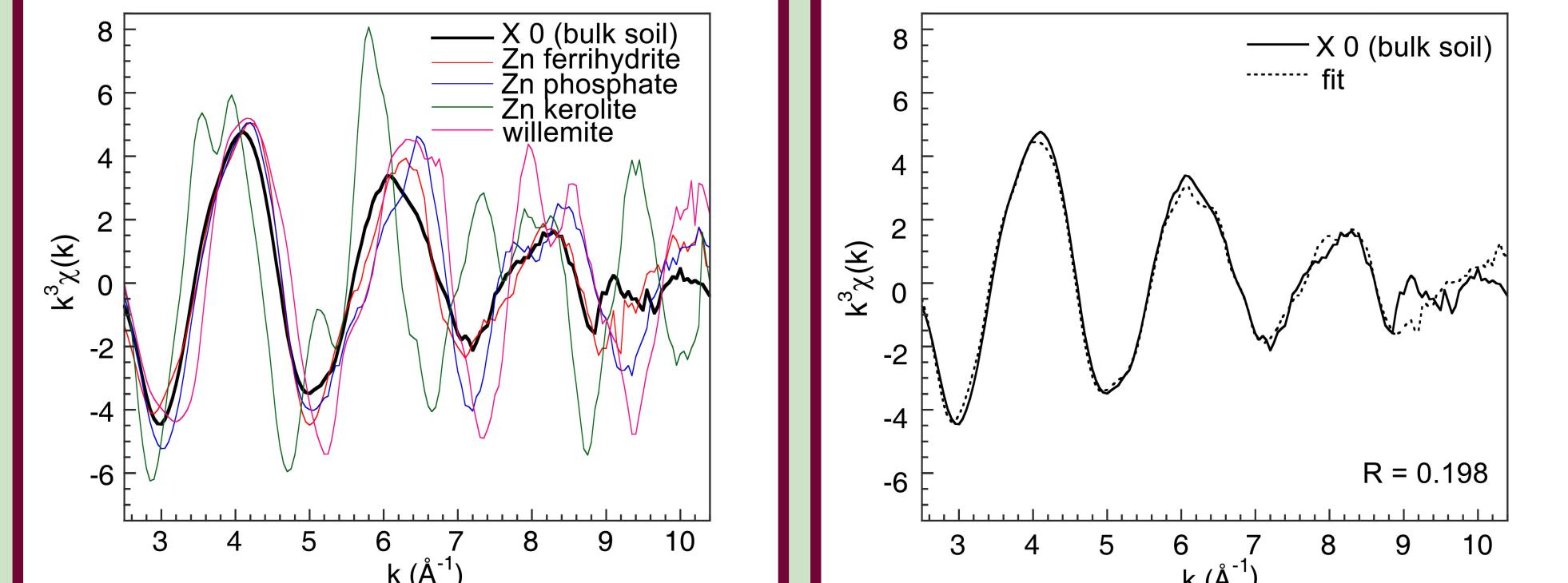
Five Zn species were positively identified at the micrometer scale :

- IV⁺Zn-sorbed Fe oxyhydroxide (modelled by ferrihydrite)
- IV⁺Zn-containing phosphate
- IV⁺Zn-containing anhydrous silicate (willemite)
- IV⁺Zn-containing hydrous silicate (hemimorphite)
- VI⁺Zn-containing phyllosilicate (modelled by kerolite)



Proportion and Solubility of Zn Species at the macroscopic scale by EXAFS and SCE

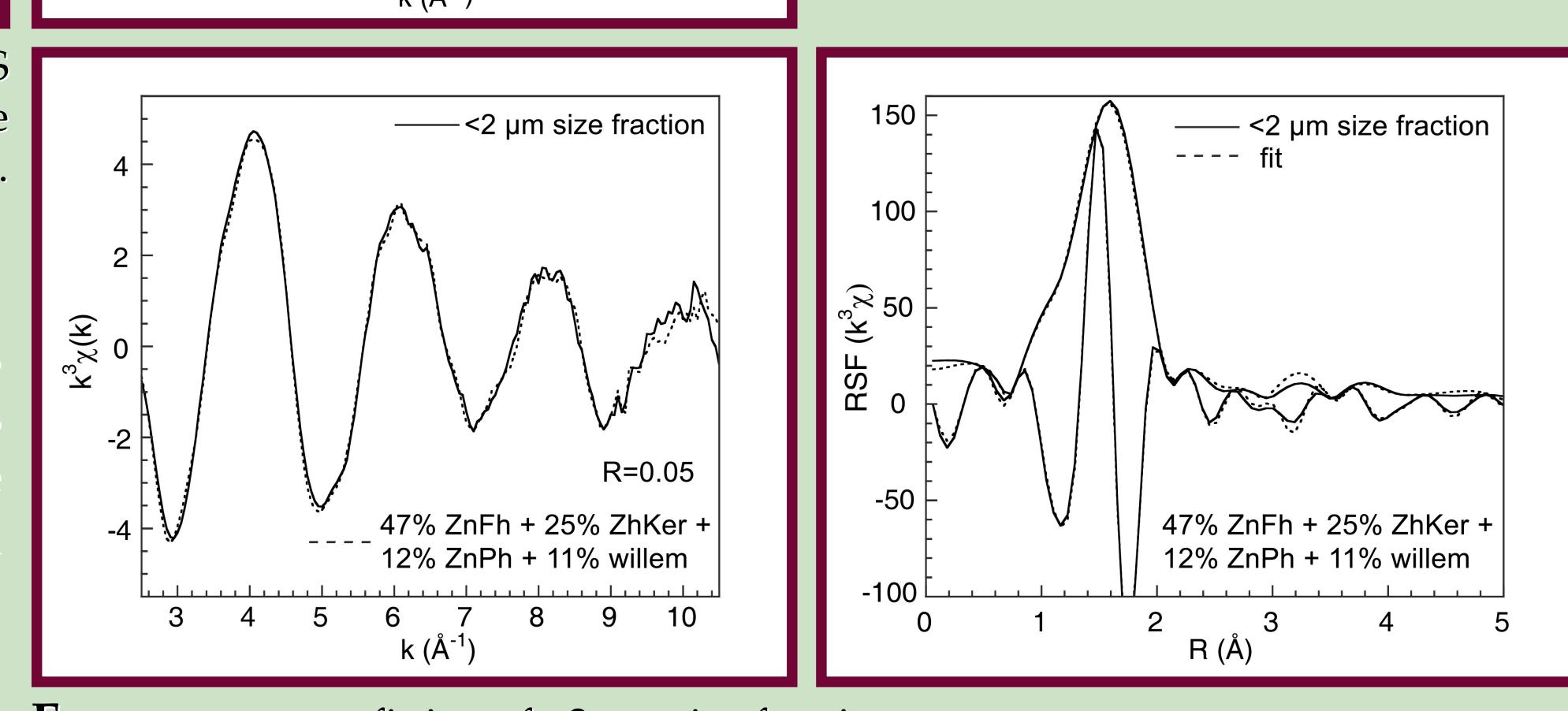
The average speciation of Zn in the bulk soil was obtained by recording EXAFS spectra on the bulk fraction.



Four-component fit of the bulk EXAFS spectrum.

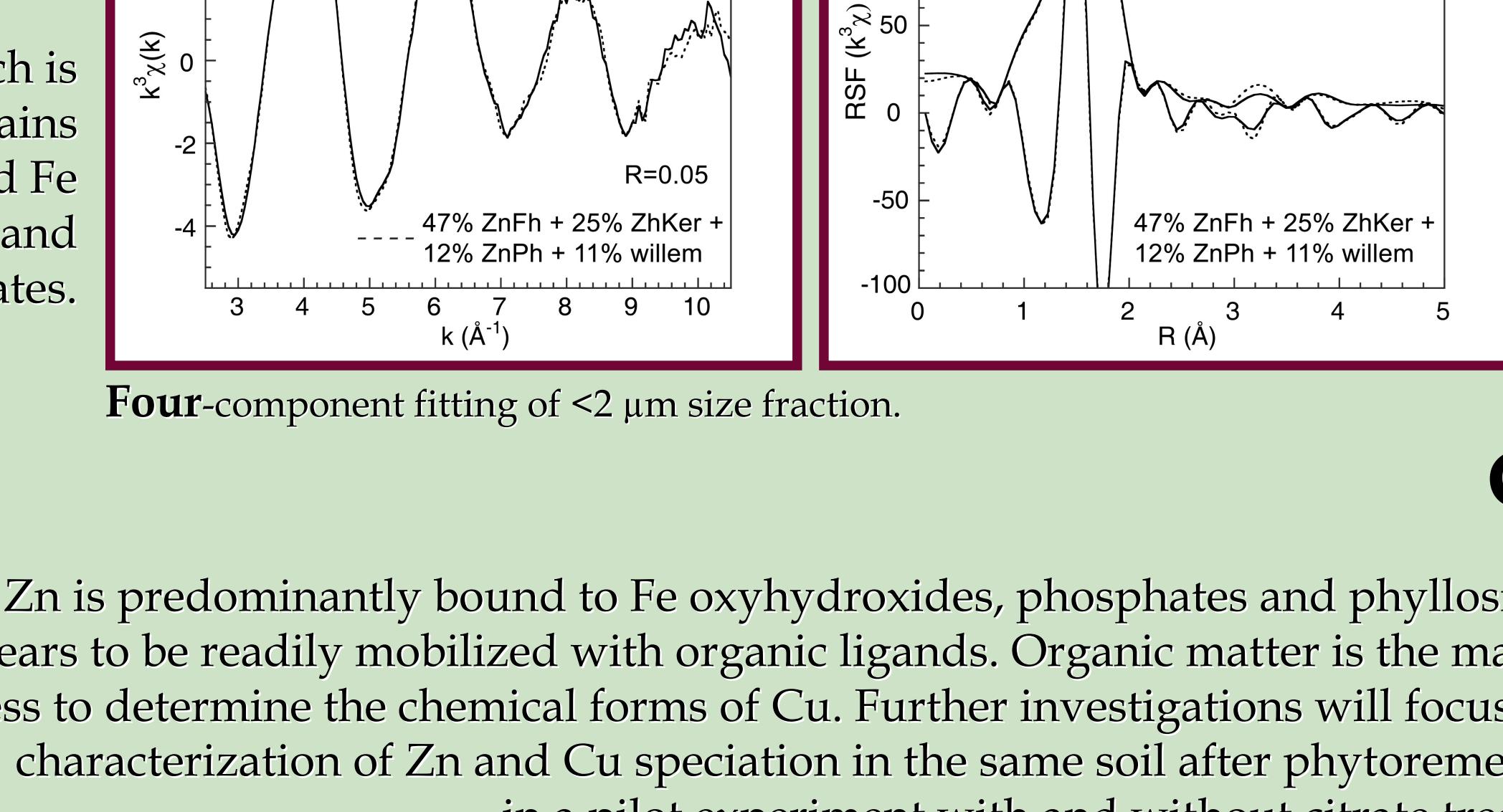
≈ 30% Zn ferrihydrite
≈ 28% Zn phosphate
≈ 24% Zn kerolite
≈ 11% willemite

Comparison of the bulk EXAFS spectrum to the four reference compounds.

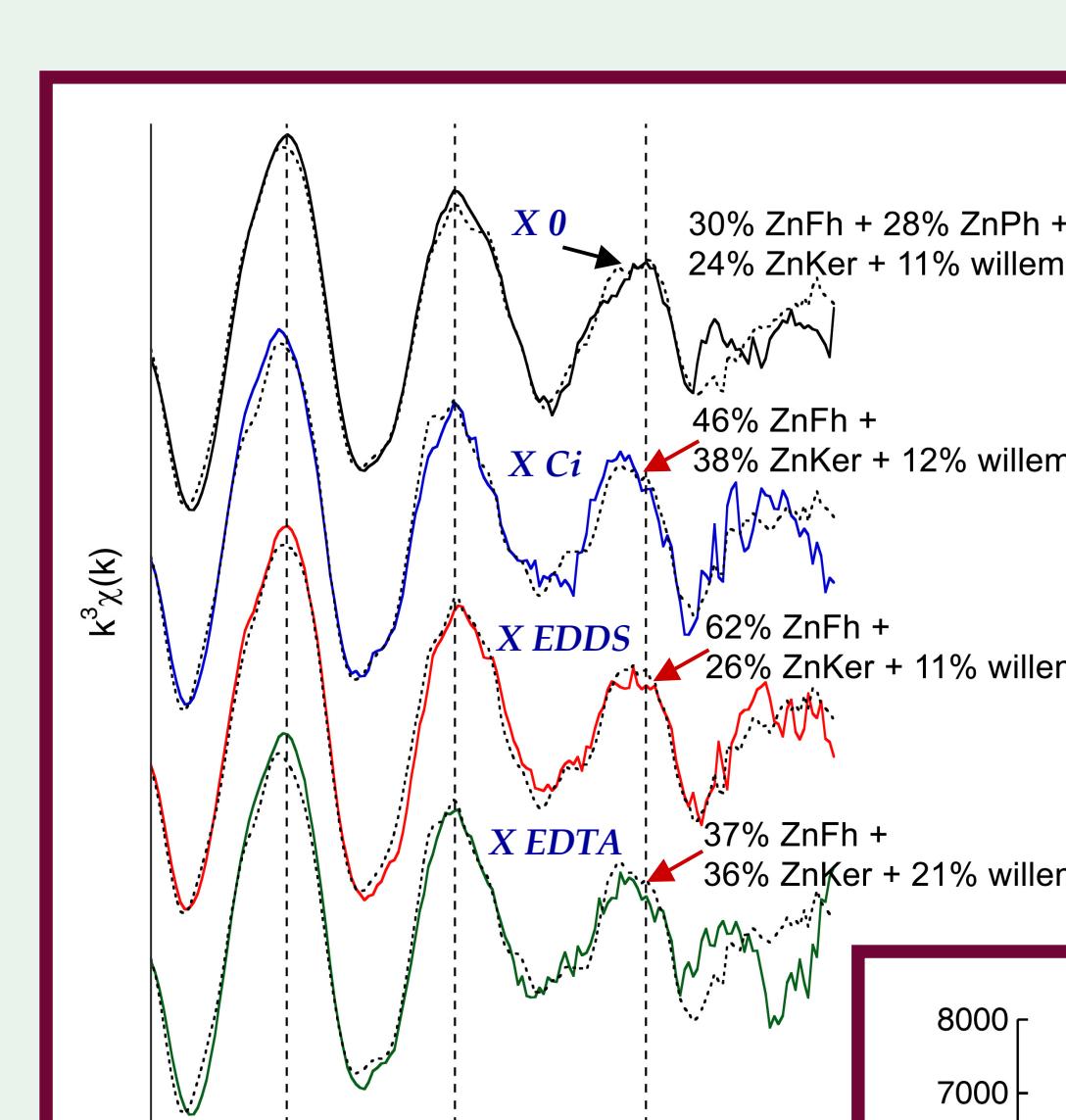


Four-component fitting of <2 µm size fraction.

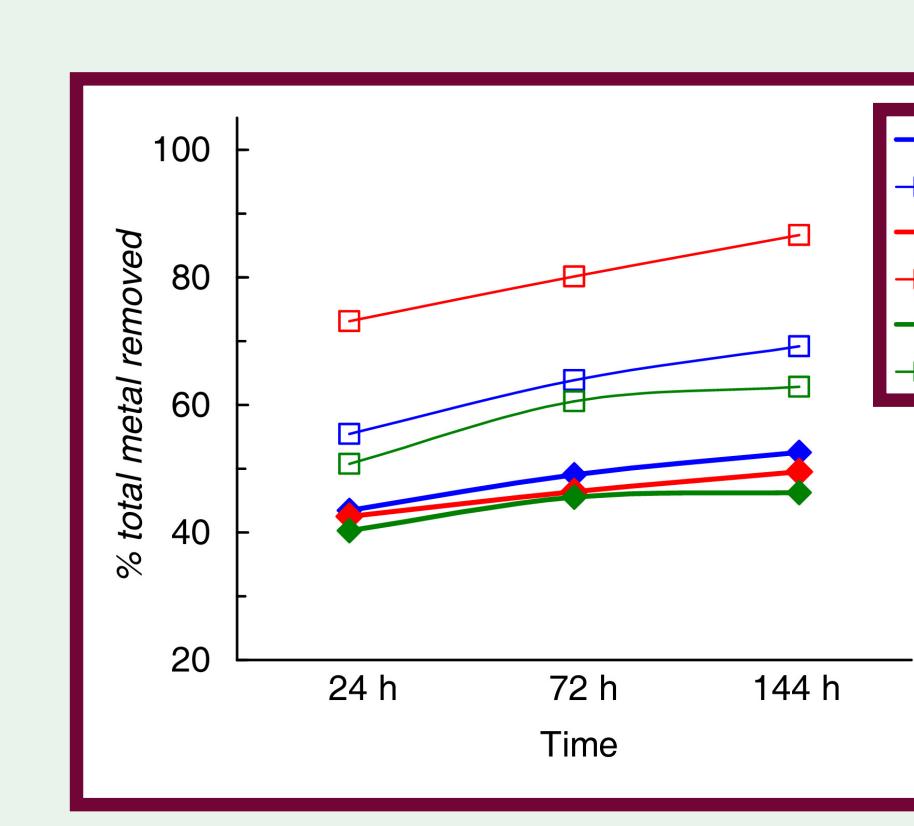
The <2 µm fraction, which is fivefold enriched in Zn, contains mostly Zn sorbed Fe oxyhydroxides and phyllosilicates.



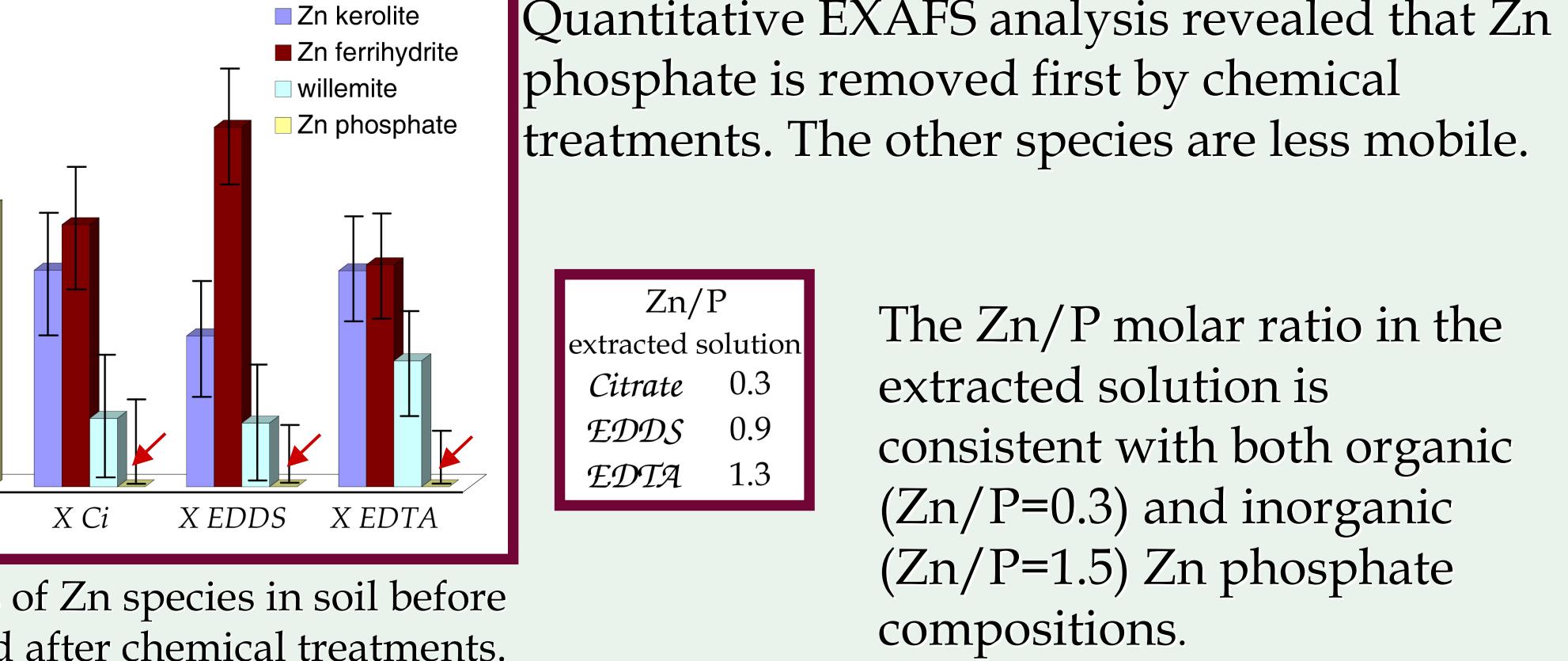
Four-component fitting of <2 µm size fraction.



Each chemical treatment induces significant changes on the EXAFS spectra.



Percentages of Zn and Cu removed as a function of extraction time and number of extraction cycles of 24 h.



Quantitative EXAFS analysis revealed that Zn phosphate is removed first by chemical treatments. The other species are less mobile.

The Zn/P molar ratio in the extracted solution is consistent with both organic (Zn/P=0.3) and inorganic (Zn/P=1.5) Zn phosphate compositions.

Conclusion

In the studied soil, Zn is predominantly bound to Fe oxyhydroxides, phosphates and phyllosilicates. Zn bound to phosphate appears to be readily mobilized with organic ligands. Organic matter is the main sink for Cu. Studies are in progress to determine the chemical forms of Cu. Further investigations will focus on the characterization of Zn and Cu speciation in the same soil after phytoremediation in a pilot experiment with and without citrate treatment.

The combination of micrometer scale (µSXRF and µEXAFS) and macroscopic scale (EXAFS) spectroscopic analysis with complementary chemical treatments provides detailed information on metal speciation in complex multi-phase environmental systems, and on the nature of the more labile metal species.

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